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Wear behavior of electroless Ni-P coatings in brine solution and optimization of coating parameters

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Abstract

The present paper studies the wear behavior of electroless Ni-P coating in brine medium and optimization of the coating process parameters for minimum wear using Taguchi method based on L_{27} orthogonal array. The study is carried out using different combinations of four coating process parameters, namely, concentration of nickel source (A), concentration reducing agent (B), bath temperature (C) and annealing temperature (D). The wear tests are conducted with a pin-on-disk Wear & Friction Monitor. The optimum combination of process parameters for minimum depth of wear is obtained. ANOVA is performed to find out the significance of the coating parameters and their interactions. The surface morphology and composition of coatings are studied with the help of scanning electron microscopy (SEM), energy dispersed X-ray (EDX) analysis and X-ray diffraction (XRD) analysis. It is found that Ni-P coating is amorphous in as-deposited condition but gradually turns crystalline with heat treatment. The worn surface morphology reveals abrasive as well as corrosive wear mechanism.

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Keywords: Electroless Ni-P coating, sliding wear, brine medium, Taguchi method, optimization

1. Introduction

Coating process is the most popular method of surface engineering for protecting the base material against wear and corrosion. Coating deposition is generally carried out in an aqueous medium by electrolytic or electroless method. In recent years, electroless methods have been well recognized and are being applied in many industrial and

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special applications where electrolytic method is inconvenient. The electroless plating deposition was proposed by Brenner and Riddell in 1946 [1,2]. Electroless nickel coatings are used in different areas such as aerospace, aviation, automotives, oil and gas processing, food processing, microelectronics, radio electronics, computer engineering, chemical processing, textiles, machinery, mining and metallization of plastic etc [3,4]. Electroless Ni-P coatings have found extensive use in surface engineering due to their excellent mechanical, physical, electrical, corrosion and tribological properties [5,6]. The mechanical and tribological properties of Ni-P coatings can further be improved by the incorporation of hard particles, with the help of heat treatment [7-9] and dry lubricants [10,11]. Wear behaviour of electroless Ni-P coatings has been studied by many researchers. Wear performance of electroless Ni–P coating is greatly enhanced with heat treatment, the treatment performed at 400^{o}C for 1 h having the highest hardness [12]. As harder materials generally encounter lesser wear, heat treated Ni-P coatings are found to be more wear resistant than the as deposited ones. Electroless Ni-P coatings are used in different environmental conditions. Typically it finds wide range of application in marine atmosphere. The present study considers the wear behavior of the coating in brine solution and optimization of coating process parameter for minimum wear based on Taguchi methodology. The characterization of the coating is done with the help of scanning electron microscopy, energy dispersive X-ray analysis and X-ray diffraction analyzer.

2. Taguchi method

In the present study, Taguchi method [13,14] is used based on orthogonal array (OA) that reduces the number of experiments required for the purpose. Thus time and cost of experimentation is decreased. Taguchi method uses S/N (Signal/Noise) ratio to identify the quality characteristics. Based on the criteria of the experiment, S/N ratio can be categorized as: lower the better (LB), higher the better (HB) and Nominal the best (NB). For the present study of wear minimization, lower the better criteria is used. Furthermore, a statistical analysis of variance (ANOVA) is performed. With the use of both S/N ratio and ANOVA analysis, the optimal combination of coating parameters is predicted.

3. Details of experiment

3.1. Deposition of coating

Electroless Ni-P coating (EN) is deposited on mild steel (AISI 1040) substrate of size 4 mm diameter ×30 mm long. Turning, parting and grinding process are used for the preparation of the solid cylindrical specimens. The substrates before coating are subjected to pickling treatment in dilute (18%) hydrochloric acid for one minute to ensure the removal of surface layer formed like rust or other oxides. Subsequently, the samples are rinsed in distilled water followed by methanol cleaning prior to coating. The selected bath composition and operating condition of electroless Ni-P coatings is enlisted in Table 1.

Table 1. Ingredients of electroless bath and their ranges

Sl. No.	Parameters	Range of parameters
1	Nickel sulphate	15 – 25 g/l
2	Nickel chloride	15 – 25 g/l
3	Sodium hypophosphite	10 – 24 g/l
4	Sodium succinate	12 g/l
5	Deposition temperature	80 – 90^{o}C
6	pH of solution	4.5

EN deposition is carried out using nickel sulphate and nickel chloride as the source of nickel, sodium hypophosphite as the reducing agent and sodium succinate as the stabilizer. The concentration of stabilizer used in baths is kept fixed. The pH value of the bath is maintained at a fixed value by adding required quantity of dilute hydrochloric acid. The cleaned samples are activated in palladium chloride at 55^{o}C temperature and placed in the bath for deposition. The coating is carried out for a period of 4 hours. After 2 hour of deposition, the specimen is taken out and rinsed with distilled water and then again placed in a freshly prepared bath for another 2 hour. This is done to get considerable coating thickness which is necessary for carrying out the tribological tests on the coating.

Deposition time is kept constant for all specimens so that the coating thickness remains approximately constant and the average coating thickness is found to be around 50 µm. After coating is over, the samples are washed with distilled water. The coated samples are annealed in a box furnace for 1 hour at different temperature (300°C, 400°C, and 500°C) according to the L_{27} OA. `

3.2. Design of experiment

Design factors are those which are varied during the experimental tests. There are number of design factors that can affect wear behavior of electroless Ni-P coatings. In this study, design factors and their levels are shown in Table 2. It is a four-factor three-level experiment, so the total degree of freedom (DOF) considering the individual factors and their interaction is 20. Here, L_{27} OA is chosen as it satisfies all the DOF conditions. The selected array requires the execution of 27 experiments. The factors (A, B, C and D) and their interactions (A×B, A×C and B×C) are assigned to their respective positions in the OA. Here, wear depth of Ni-P coating is taken as the response variable.

Table 2. Design factors and their levels

Design factors	Unit	Levels		
		1	2	3
Concentration of source of nickel (A)	(g/l)	30	40	50
Concentration of reducer agent (B)	(g/l)	10	17	24
Deposition temperature (C)	°C	80	85	90
Annealing temperature (D)	°C	300	400	500

3.3. Wear test

Wear behaviour of Ni-P coated specimens are carried out in brine medium (3.5 % NaCl solution) at ambient temperature of about 28°C. Wear tests are conducted in Wear & Friction Monitor (TR-208-M2, Ducom, India) using a pin-on-disk configuration. A pictorial view of the Wear & Friction Monitor is shown in Fig. 1. The coated specimens serve as test specimens which are held perpendicular against a rotating alumina disk (100 mm dia × 8 mm thickness). Microhardness of alumina disk is 1680 HV_1, which is higher than the microhardness of Ni-P coated specimen (average microhardness value is 700 HV_1). Thus wear will take place only in test specimens. Normal load is applied by placing dead weights on loading pan. The depth of wear is measured by a LVDT (Syscon) which has a measurement range of ±2 mm. The experiments are conducted with a constant load of 20 N as well as wear track dia of 40 mm and at 50 rpm and for a constant time of 10 min considering the small coating thickness. Experimental data of wear test is shown in Table 3.

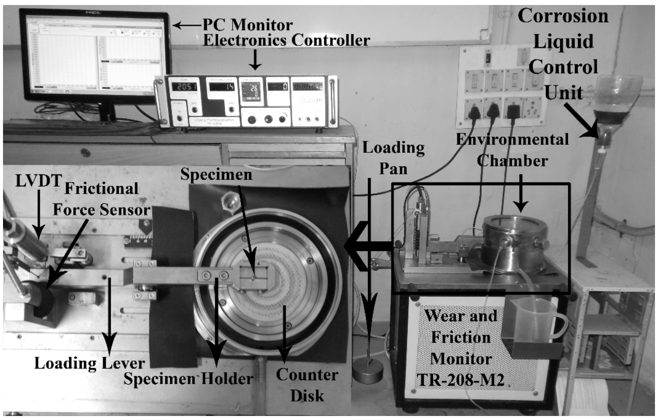

Fig. 1. pictorial view of wear & friction monitor

Table 3. Values of wear depth and their corresponding S/N ratio

Exp. No	Wear depth (μm)	S/N ratio (dB)	Exp. No	Wear depth (μm)	S/N ratio (dB)	Exp. No	Wear depth (μm)	S/N ratio (dB)
1	20.18	-26.0984	10	12.26	-21.7698	19	20.75	-26.3404
2	11.33	-21.0846	11	40.79	-32.2111	20	34.29	-30.7033
3	14.26	-23.0824	12	36.32	-31.2029	21	13.78	-22.785
4	34.43	-30.7387	13	12.06	-21.6269	22	12.45	-21.9034
5	30.01	-29.5453	14	34.56	-30.7715	23	20.05	-26.0423
6	47.44	-33.5229	15	9.41	-19.4718	24	22.72	-27.1282
7	22.10	-26.8878	16	29.21	-29.3106	25	16.27	-24.2278
8	48.50	-33.7148	17	15.01	-23.5276	26	30.31	-29.6317
9	10.42	-20.3574	18	35.26	-30.9456	27	11.22	-20.9999

3.4. Surface morphology and composition study

Surface morphology study of the coating is done by SEM (JEOL, JSM-6360) to analyze the microstructure of the deposited coatings before and after annealing at various temperatures. SEM is also done after tribological testing to see the wear track patterns. EDX analysis (Inca, Oxford) is done in conjunction with SEM to study the composition of the Ni-P coatings in terms of the percentages of nickel and phosphorous. The phase structure is studied with the help of X-ray diffraction (XRD) analysis (Rigaku, Ultima III) so that different precipitated phases both pre and post heat treatment are identified.

4. Results and discussion

4.1. Analysis of signal-to-noise ratio

In respect of DOE, signal is interpreted as desirable value (mean) and noise is interpreted as undesirable value (standard deviation). Taguchi employs S/N ratio to convert the experimental results into a value for the evaluation characteristic in the optimum parameter analysis. In the present work, S/N ratio analysis is used considering depth of wear as the performance index. As wear depth is to be minimized, the S/N ratio for wear is calculated using LB (Lower the better) criterion. Table 3 shows the experimental wear values and the corresponding S/N ratio. The average of S/N ratio of each level of the factors of A, B, C and D is given in Table 4 and total average value of S/N ratio of all the 27 experiment is also listed in this Table. From Table 4 and Fig. 2, it is found that process parameter D is the highest delta value (rank 1). Hence, annealed temperature has done the more effective roll play for wear of electroless Ni-P coatings surface [12]. Parameter C is also found to have some influence over the wear. But parameters A and B have the least influence over the wear behavior of the coating. From the Fig. 3, it can be seen that there is strong interaction of parameters A Vs B. Parameter A Vs C and B Vs C are found as a moderate interaction. The optimal combination of parameter is found to be A3B1C1D2.

Table 4. Response table for mean S/N ratio

Level	A	B	C	D
1	-27.23	-26.14	-25.43	-28.69
2	-26.76	-26.75	-28.58	-23.33
3	-25.53	-26.62	-25.50	-27.49
Rank	3	4	2	1
Delta	1.70	0.61	3.15	5.36

Total mean S/N ratio = -26.50 dB

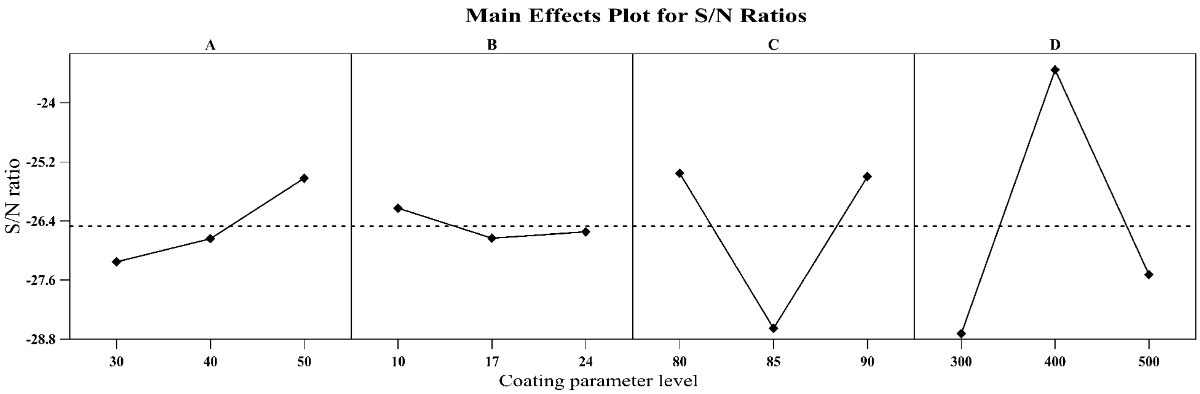

Fig. 2. main effects plot for signal-to-noise ratio

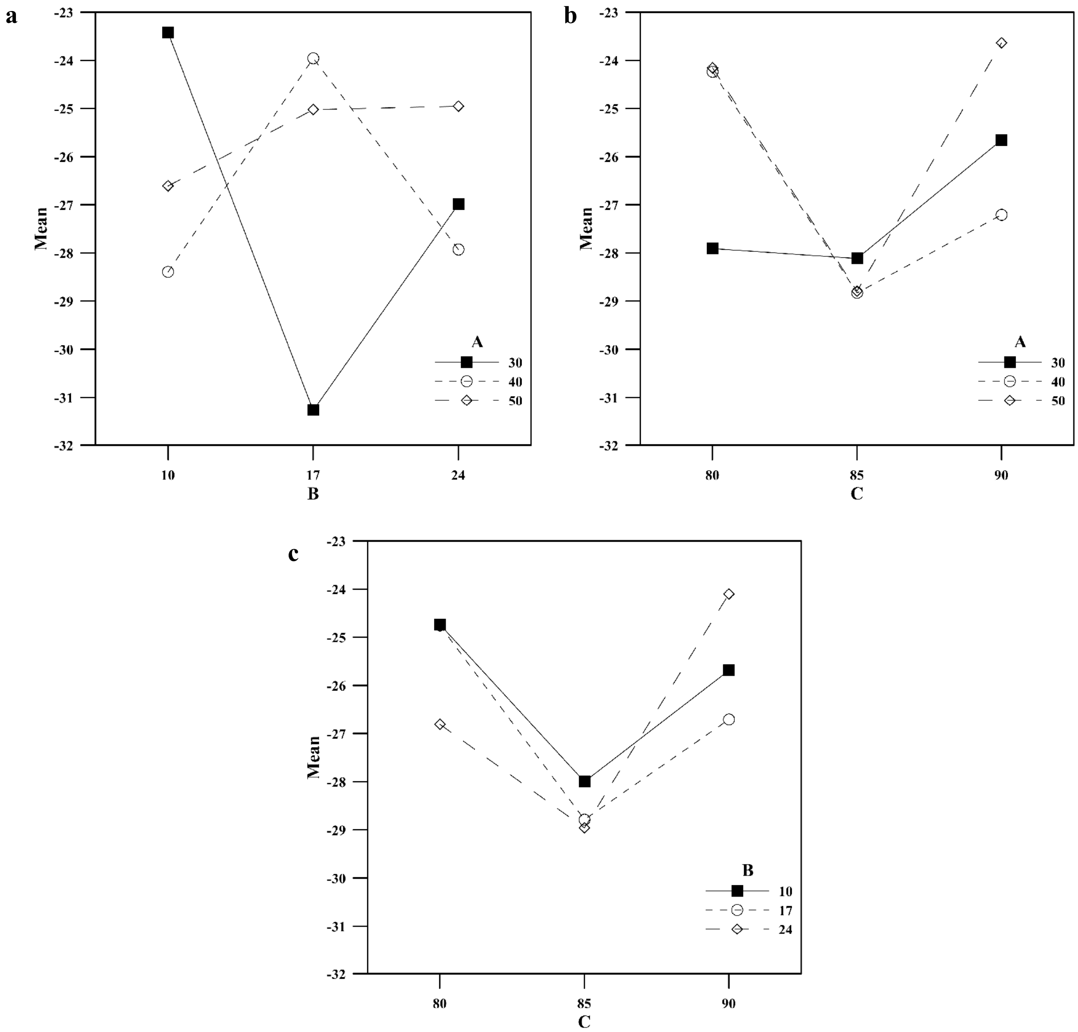

Fig. 3. interaction plot for mean S/N ratio (a) A vs B (b) A vs C and (c) B vs C

4.2. Analysis of variance (ANOVA)

The idea of the analysis of variance is to find out the significance of process parameters and also the percentage contributions of the factors and the interactions in affecting the response. From Table 5, it can be observed that parameter D has the significant parameter with confidence level of 90%. From ANOVA, the percentage contribution of the factors and interactions are also calculated. Here, parameter D has the largest contribution. Similarly, the parameter A, C, as well as interactions A×B, A×C and B×C have moderate contribution while parameter B has almost no contribution within the experimental range considered in the study.

Table 5 Results of ANOVA for wear depth

Source	DOF	Sum of square	Mean square	F	Contribution (%)
A	2	13.83	6.92	0.37	2.71
B	2	1.85	0.93	0.05	0.36
C	2	58.23	29.11	1.58	11.39
D	2	142.26	71.13	3.85*	27.83
A*B	4	131.72	32.93	1.78*	25.77
A*C	4	33.93	8.48	0.46	6.64
B*C	4	18.58	4.64	0.25	3.64
Error	6	110.71	18.45		21.66
Total	26	511.11			

*Significant factors and interactions $F_{0.1,2,6} = 3.46$; $F_{0.25,4,6} = 1.78$

4.3. Confirmation test

After the optimal level of testing parameters have been found, it is necessary that verification test is carried out in order to evaluate the accuracy of the analysis and to validate the experimental results. The estimated S/N ratio, $\hat{\eta}$ using the optimal level of the testing parameters can be calculated as:

$$\hat{\eta} = \eta_m + \sum_{i=1}^{0} (\overline{\eta}_i - \eta_m) \tag{1}$$

Where, η_m is the total mean S/N ratio, η_i is the mean S/N ratio at the optimal testing parameter level and o is the number of main design process parameters that significantly affect the wear characteristics of Ni-P coating under NaCl solution. Table 6 shows the comparison of the estimated S/N ratio with the actual S/N ratio using the optimal parameters. The improvement of S/N ratio from initial to optimal condition is 3.23 dB, which means wear depth is reduced by about 31 % and it is a significant improvement.

Table 6 Results of confirmation test

	Initial condition	Optimal condition	
		Prediction	Experimentation
Level	A2B2C2D2		A3B1C1D2
Wear depth (μm)	20.67		14.26
S/N ratio (dB)	-26.31	-23.33	-23.08

Improvement of S/N ratio = 3.23 dB

4.4. Surface morphology and compositional study

The coated specimens as-deposited as well as heat treated at different temperatures are studied by SEM. From the

SEM, [Fig. 4(a)] micrographs of the surfaces it is seen that there are many globular particles on the surface of the substrate. The surface is optically smooth and of low porosity. No obvious surface damage is found [5]. Fig. 4(b) shows the SEM micrograph of the coating surface after wear testing. From the SEM micrograph it is observed that the worn surface is composed of mainly irregular grooves all over the whole surface. EDX analysis [Fig. 5] shows that coating contains in weight 91.56 % Ni and 8.44 % P. Fig. 6 shows the XRD plots of as deposited and heat treated conditions. From this figure, it is evident that in as-deposited condition the phase is mostly amorphous but turns to crystalline [4,9] with heat treatment because various nickel phosphide compound (Ni_2P, Ni_3P and Ni_5P_2) are found in heat treated specimen.

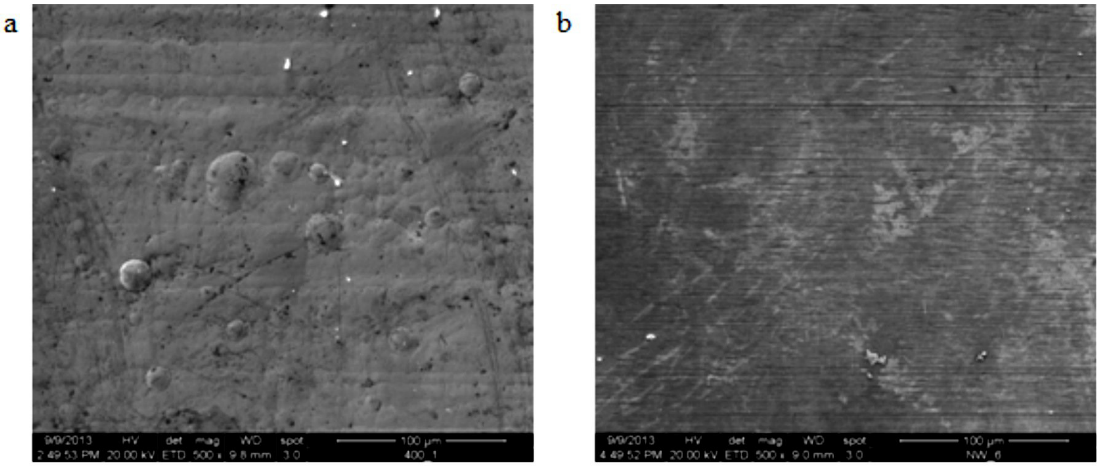

Fig. 4. SEM pictures of Ni-P coatings: (a) before wear test and (b) after wear test.

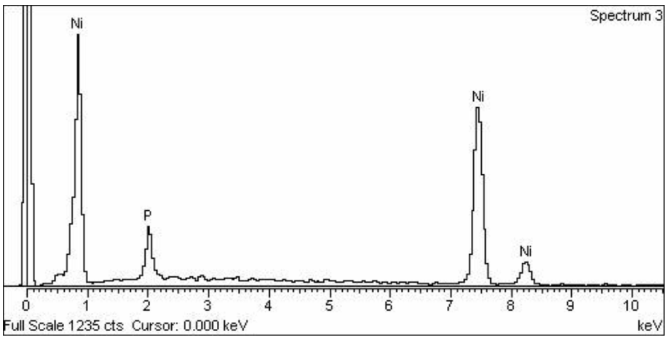

Fig. 5. EDX spectra of Ni-P coatings

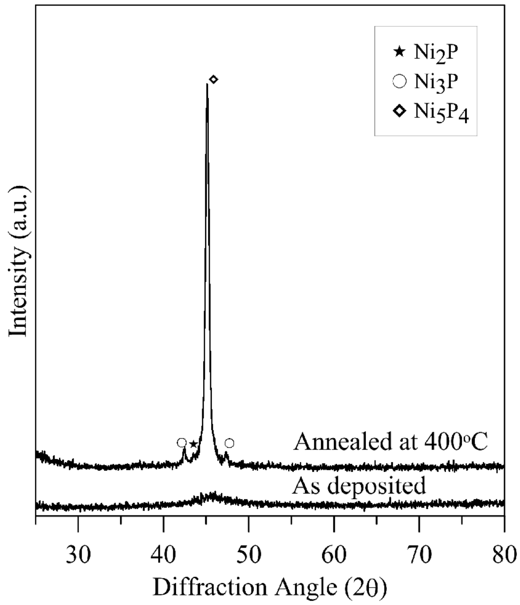

Fig. 6. XRD plots for Ni-P coatings

5. Conclusion

In the present study, Taguchi method is employed to optimize the coating process parameters for minimum wear of electroless Ni-P coatings in brine solution against rotating alumina disk. It is seen that annealing temperature has the most significant influence in controlling wear characteristics of electroless Ni–P coating. The interaction of nickel source concentration and reducing agent concentration has some significant influence. The optimal coating parameter combination for minimum wear is obtained as A3B1C1D2 i.e, highest levels of nickel source concentration, lower level of reducing agent concentration and bath temperature along with middle level of annealing temperature. The wear depth is reduced by about 31% from initial to optimal. It is observed that surface of the coatings is smooth, of low porosity and dense with nickel and phosphorous content of around 91.5% and 8.5% respectively. The coatings are amorphous in as-deposited condition but after heat treatment, the coating turns to crystalline with different nickel phosphide compounds.

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